AMMONIA-FREE NOx CONTROL SYSTEM

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APRIL 1 THROUGH JUNE 30, 2004

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TECHNICAL PROGRESS REPORT NUMBER 41865R3
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Abstract

Research is being conducted under United States Department of Energy (DOE) Contract DE-FC26-03NT41865 to develop a new technology to achieve very low levels of NOx emissions from pulverized coal fired boiler systems by employing a novel system level integration between the PC combustion process and the catalytic NOx reduction with CO present in the combustion flue gas. The combustor design and operating conditions will be optimized to achieve atypical flue gas conditions. This approach will not only suppress NOx generation during combustion but also further reduce NOx over a downstream catalytic reactor that does not require addition of an external reductant, such as ammonia.

This report describes the work performed during the April 1 to June 30, 2004 time period.

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1. Executive Summary

1.1 Project Overview

State-of-the-art NOx control technology for pulverized coal (PC) steam plants involves a combination of low NOx combustion and selective catalytic reduction (SCR) technologies. Development of these systems has approached a plateau and further improvements will likely be incremental. To advance NOx control technology to the next level, new concepts must be considered.

The objective of this project is to evaluate the viability of a novel integration between the PC combustion process and flue gas NOx reduction. The concept exploits the relationship between CO and NOx both in the combustion and flue gas NOx destruction processes to achieve very low levels of NOx from the boiler system without adding any external reductant, such as ammonia, typically used for SCR processes.

The project starts with a review and evaluation of existing NOx reduction and CO oxidation catalysts, including those catalysts formulations successfully used in the automotive applications, for their use in PC power plants. This knowledge, combined with prior catalyst research for power plant applications conducted at Lehigh University will allow the research team to identify and test catalyst formulations robust enough for power plant flue gas environments and which can achieve competitive NOx reduction performance and economic targets.

A detailed PC combustion study, applying computational fluid dynamics simulation program to performed boiler and burner design modeling, will complement the catalyst study by investigating ways to optimize the combustion process for the lowest NOx formation while generating sufficient levels of CO needed by the downstream catalytic NOx reduction process. Furnace configuration, air staging, and burner design will be optimized in this process.

The study will then focus on the comparative evaluation of a conceptual, 400 MWe, coal-fired PC boiler system, utilizing this novel NOx control concept. For this evaluation, the concept plant will be compared to a traditional PC boiler configured with current low NOx combustion commercial technology and an ammonia-based SCR system. The comparison will involve conceptual level design of the furnace and catalyst reduction system to obtain equipment pricing, operational costs, performance data as well as qualitative reliability information.

1.2 Progress During the Quarter

The project work during this quarter was focused on Task 2 - Catalyst Testing. The goal of Task 2 was to screen and characterize candidate catalyst samples conceived and selected through in-depth literature study and development work by the project team.

A short list of candidate catalysts was identified for Task 2 testing. The first group of test catalyst samples (activated carbon-based, multi-metal oxide catalysts) were prepared by aqueous incipient impregnation method and tested on the bench scale catalyst test rig at Lehigh University.

Tests with various combinations of Fe, Cu, and Ce on activated carbon support were carried out under a wide range of conditions simulating real life coal-fired power plants. In total, more than 10 catalysts have been prepared and tested. To ensure repeatable results, multiple tests were done for most of these catalysts, with each test usually lasting a day. The test results are discussed in following sections.

Very promising data were obtained during this quarter's testing. Most of catalysts exhibited high catalytic reactivity with NO conversion reaching 80-90% at relatively low temperatures, and with little or no N_2O formation. Some catalysts also achieved CO reduction as high as 85-90% for a wide range of operation temperatures, especially at low temperatures. Data analyses also revealed that the performance of the NO - Catalyst - CO system was determined by four main competing reaction pathways, as follows,

1. Direct reduction of NO by CO, either added in test gas or generated thru pathway 3.
2. Destruction / oxidation of excess CO.
3. Partial combustion / gasification of supporting activated carbon.
4. Direct reaction of NO by carbon.

Depending on reaction temperature and type(s) / amounts of metal applied on catalyst, different reaction pathways may dominate the performance under given operating conditions.

As of the end of this quarter, Task 2 – Catalyst Testing and Evaluation - is still ongoing. We will continue the Task 2 work in the third quarter of 2004 to have more catalysts tested and more data available and analyzed to support Task 3 - Furnace Optimization, which will also start during the third quarter.

2. Experimental

2.1 Test Rig

A fixed bed reactor at Lehigh University was the main experimental tool employed in this study. The catalyst testing system featured a vertical down flow quartz tube reactor (10.5mm ID x 13 mm OD). Temperature in the reactor was monitored by an axial thermocouple generally 2.5-3.5 cm below the top of the catalyst bed (in the catalyst bed). The variation of thermocouple location results from each catalyst being packed in the reactor tube differently (and some tended to compact upon use). Gas stream heating was accomplished with a vertical split-tube furnace surrounding the reactor. The gas stream inlet and outlet 316 stainless steel sections were wrapped with heating tapes and insulation and heating was controlled by two Variances. Temperatures of the inlet and outlet lines were monitored by six thermocouples and maintained above 100^{o}C.

Figure 1 is a process flow diagram of the NO reduction test rig. Figure 2 shows the rig with the furnace open with a quartz tube reactor inside. Approximately 20 ml of catalyst sample is placed in the reactor, quartz wool plug. Based on literature survey, the CO-NO reaction under study is not catalyzed by the quartz reactor tube at temperatures below 1000°C. Individual gas flow meters are used to regulate flow rates from gas cylinders containing O_2, NO, SO_2, CO, CO_2 and N_2 which are mixed to simulate flue gas from coal-fired power plants. A cylinder pump is used

to inject the desired amount of distilled water through a vaporizing pipe section into the inlet gas pipe to the reactor. The outlet test gas passes through a chiller before entering the gas analyzers. A bypass valve can be used to connect the inlet gas stream directly to the analyzers to confirm the inlet concentrations of NO and other gases. A bubble flow meter is used to calibrate the rotameters for individual gas streams.

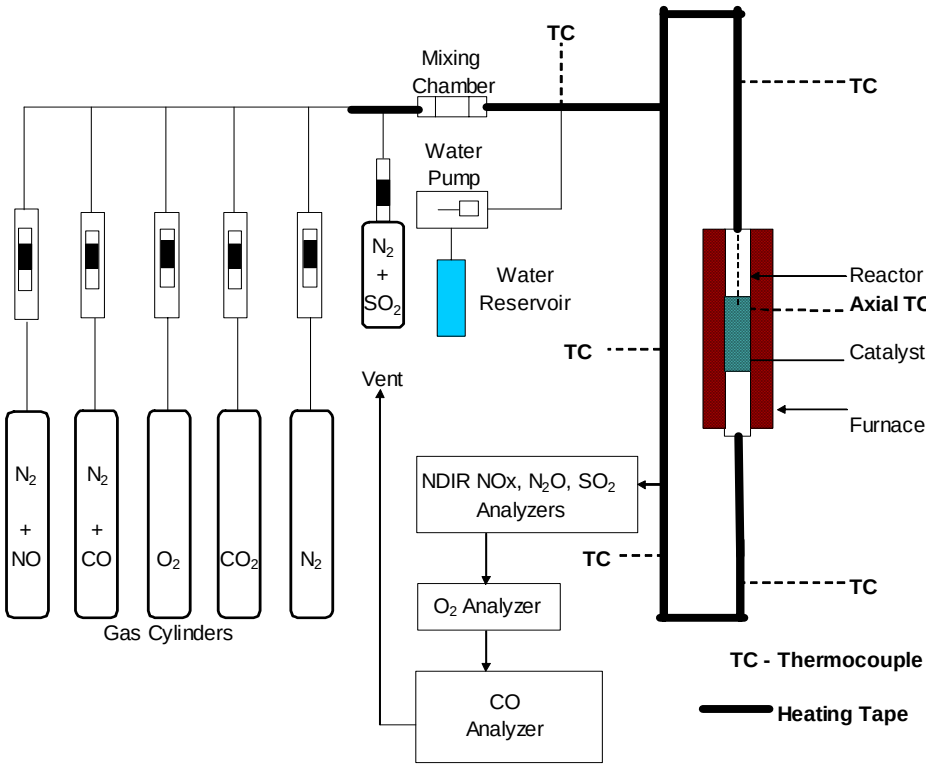

Figure 1 Bench Scale NOx Testing System

Outlet NO, N_2O, SO_2 concentrations were analyzed by Siemens Ultramat 6 NDIR analyzers. O_2 was analyzed by a Siemens Oxymat 6 Paramagnetic analyzer. CO was determined by a Testo 325-3 digit CO analyzer. Monitoring of these gases in the reactor inlet and outlet streams was carried out to determine if these components of the gas mixture were being generated or consumed. CO_2, moisture and SO_2 concentrations were calculated based on their flow rates into the reactor.

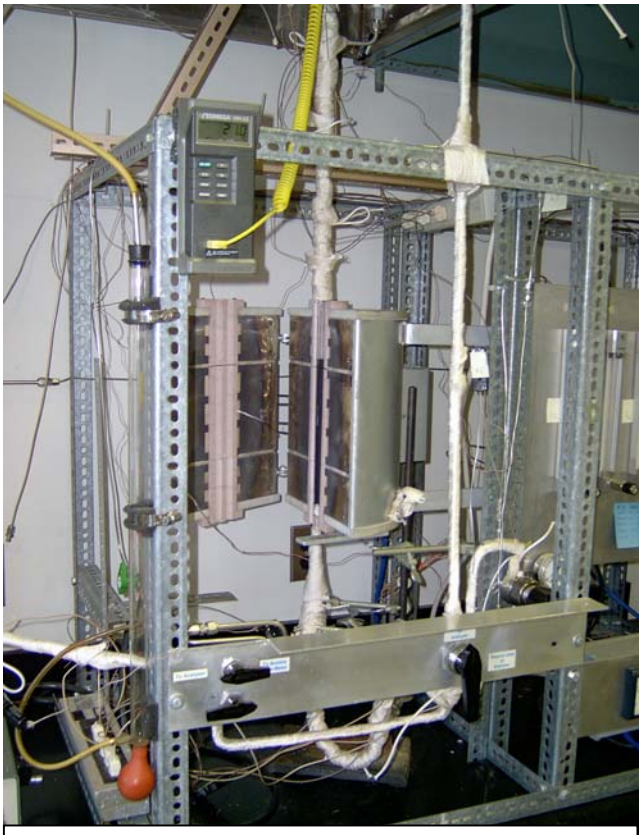

Figure 2 Photo of Test Rig

2.2 Catalyst Preparation

The 12-20 Mesh size activated carbon, which was derived from lignite, was purchased from Aldrich and was designated as Darco Activated Carbon obtained from American Norit Co. Due to its relatively low cost, lignite based activated carbon has been widely used in the waste to energy industry for trace pollutant removal, and is currently being demonstrated to capture mercury for coal fired utility plants. The BET surface area of an "as received" sample was determined (6-point analysis) by nitrogen adsorption at -196°C using a Micromeritics Gemini 2360 V1.03 instrument. Before analysis, the sample was purged with flowing N_2 while heating from 60°C to 200°C over a period of 55 min. The sample was then maintained at 200°C for 2 hr and cooled to ambient temperature. During this thermal treatment, the sample exhibited a 1.5% weight loss. The measured surface area of the activated carbon was 525 m^2/g. After loading of the catalytic components the surface area for catalyst Type B became 468 m^2/g, which is very close to that of the as received activated carbon (AC).

The catalysts were prepared by impregnation method. Reagent grade chemicals of metal nitrates from Fisher Scientific (ACS Certified) or Strem Chemicals were dissolved in distilled water and heated to 60°C. To the solution was added AC while maintaining constant stirring. The solution was then evaporated over a period of a few hours, and when the solid was dry to the touch, it was

placed in a plastic bottle. The open plastic bottle was placed in an N_2-filled glove bag containing a beaker of Drierite desiccant.

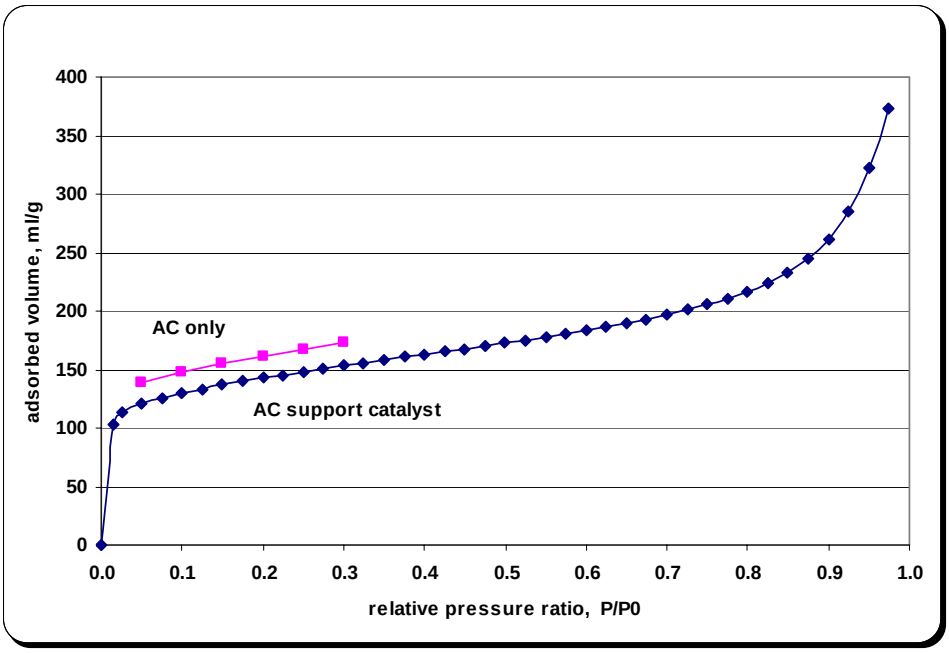

Figure 3 Determination of Surface Area by Adsorption

Activation of catalysts was carried out by decomposition of metal salts. The impregnated multi-metal nitrate salts were decomposed by heating under established flow rates of the simulated gas mixture containing 3.0% O_2, 14% CO_2, 520 ppm CO and balance N_2.

The gas hourly space velocity (GHSV) used was approximately 855 hr^{-1}. The inlet and exit lines as well as the furnace were then heated. The reactor was heated from ambient temperature to 265°C slowly over a period of approximately 3 hours and then held at this temperature for an additional 30 min. During this treatment, a large amount of NO were released from the catalyst, as a result of nitrate salt decomposition, which peaked in the temperature range of 100-200°C and then decreased with further increase of temperature and time of equilibration. CO and N_2O were also measured during decomposition / activation at increased temperatures. After the decomposition, the furnace controller was turned off and only the flow of N_2 was maintained overnight.

2.3 Catalyst Test Procedure

A portion of the catalyst was thermally treated in flowing N_2, as described above, and a weight loss of about 10-20% was observed. For catalyst Type B, its surface area was measured again by a 6-point BET method as 465 m^2/g, which was very close to the original value of as received AC. A complete adsorption isotherm was then obtained over the relative pressure range of P/P_o = 0.025-0.975, indicating micro-pore porosity but no larger meso-pore contribution. The first 11

data points yielded a BET surface area of 468 m^2/g, and this duplicate analysis indicated that no gaseous adsorbent or volatile matter was desorbing during these analyses.

For NO reduction activity determination, the flow rates of the gas mixture components were reestablished and were measured / confirmed by means of a bubble meter. The reactor was then heated and the NO/N_2 flow was turned on. The temperature of the catalyst bed was then sequentially changed to get a conversion-temperature profile both in steady state and in transient conditions. To screen the performance of different catalysts, a constant GHSV of 1050 hr^{-1} at ambient temperature and pressure and a constant inlet gas composition were used. The established reactant gas mixture consisted of the following for most of the tests,

NO	CO	O_2	CO_2	N_2
260 ppm	520 ppm	3.0 %	14.0%	83%

This gas mixture gives a CO:NO molar ration of 2.0, with enough excess for the NO reduction reaction (4). A GHSV = 1050 hr^{-1} was used for the most of catalyst screening tests. To study the catalyst reactivity for NO reduction without the interference of poisoning or inhibition, most of initial catalyst evaluation tests were carried out in gas without SO_2 and moisture. Further testing to determine inhibition and poisoning effects of SO_2 and moisture will follow these tests.

Catalytic reactivity is expressed by conversions, i.e.

NOx Conversion = $1 - (NOx)_{out} / (NOx)_{in}$
N_2O Conversion = $(N_2O)_{out} / (NOx)_{in}$
CO Conversion = $1 - (CO)_{out} / (CO)_{in}$
O_2 Conversion = $1 - (O_2)_{out} / (O_2)_{in}$

It is assumed that there is no significant difference between gas inlet and outlet molar flow rates, considering 97% of feed gas is N_2 or CO_2 that are not expected to participate in any of the reactions under study here. The NO reductions were determined following attainment of steady state. As a post-combustion NO control process, a low NO level of 260 ppm was used in this test, assuming some forms of low NOx combustion technology is being used.

The temperature of the catalyst bed was changed and the NO conversion was determined as it approached to steady state at each set point. The set point temperatures were selected to achieve the maximum NO reduction for each catalyst. The NOx conversion as a function of temperature and time were recorded. The other gases, such as O_2, CO, SO_2, and N_2O were also recorded. They are used to analyze catalytic selectivity, NOx reduction pathways, and possible side reactions, especially the relations among NOx reduction, CO depletion, and O_2 consumption. The reactivity profile of NOx reduction vs. temperature can then be plotted to compare the performance from different catalysts.

After a test, the test sample is cooled down and preserved in an N_2 environment. Most of tested catalysts were subjected to repeat test(s) under identical conditions as used for the first day test. The multi-day tests ensures data / procedure repeatability and provide clues to any deactivation over time.

Tests on various combinations of Fe, Cu, and Ce, on AC support have been conducted. To date, 10 catalysts have been prepared and evaluated.

Table 1 describes the various catalyst samples tested. The amount of each metal impregnated on the AC support is expressed as the percentage of a reference total metal loading. The test runs in this report will be reported to as a combination of letters and numbers, such as A-1, B-2, where the letter indicates the catalyst type and the number indicates the order of the test run, for example, 1 for first run.

Table 1 Catalyst Samples Tested*

Catalyst Name	First Test Date	Catalyst Formula	GHSV, 1/hr
A	04/07	As-received AC	1050
B	04/09	10% Fe/ 10% Cu	1050
C	04/21	40% Fe/10 % Cu	1050
D	04/30	10% Fe / 30% Cu	1050
E	05/21	40% Fe/ 0% Cu	1050
F	05/26	7% Fe / 7% Cu	840
G	05/29	40% Fe / 10% Cu	1050
H	06/09	40% Fe / 30% Cu	1050
I	06/22	Aqueous-treated AC	1050
J	06/29	40% Fe / 30% Cu / 20% Ce	1050

* Percentage in catalyst formula refers to a reference total metal loading.

3. Results and Discussion

3.1 Overview of Catalyst Tests

Figure 4 is an example of a typical catalyst test history. At the beginning of a test when the catalyst bed is cold, the activated carbon can adsorb approximately 85-90% of NO. When the catalyst bed reaches a temperature of about 120°C, only a slight adsorption of NO still occurs. Therefore, for most of the tests, NO was added to test gas stream only when the bed temperature reaches 150°C. Multi-day tests were carried out for most of the catalyst samples. Excellent repeatability was obtained.

Figure 5 shows the conversion data for CO, NO, and O_2. The NO conversion displayed a typical S-type curve where the catalyst reactivity rapidly increased at a rather sharp “light-off” temperature. When temperature increased further, the NOx reduction reached a maximum of about 80-90% NO conversion and then started to drop.

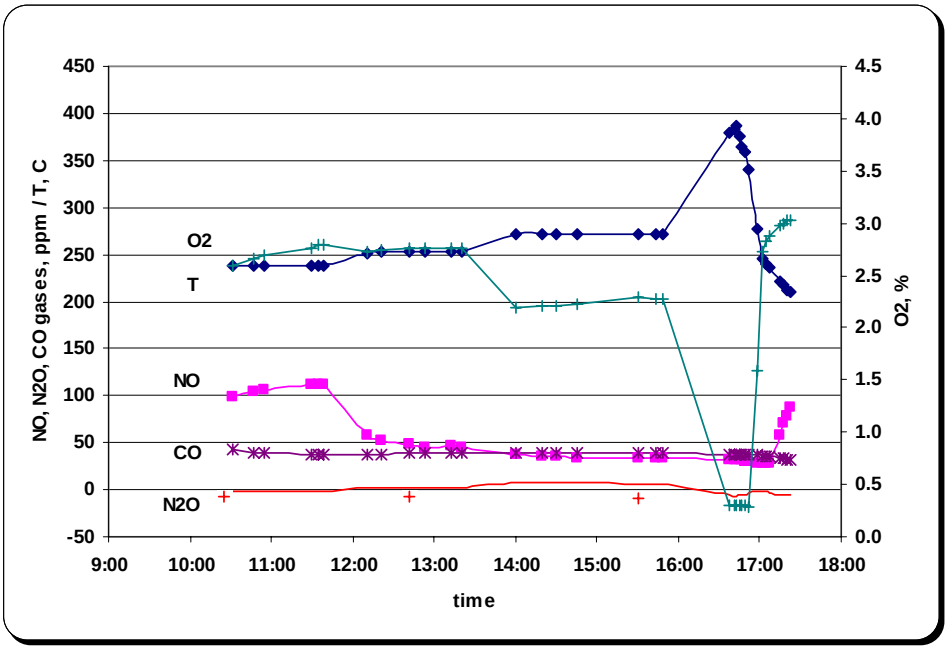

Figure 4 Typical Transient Test Data

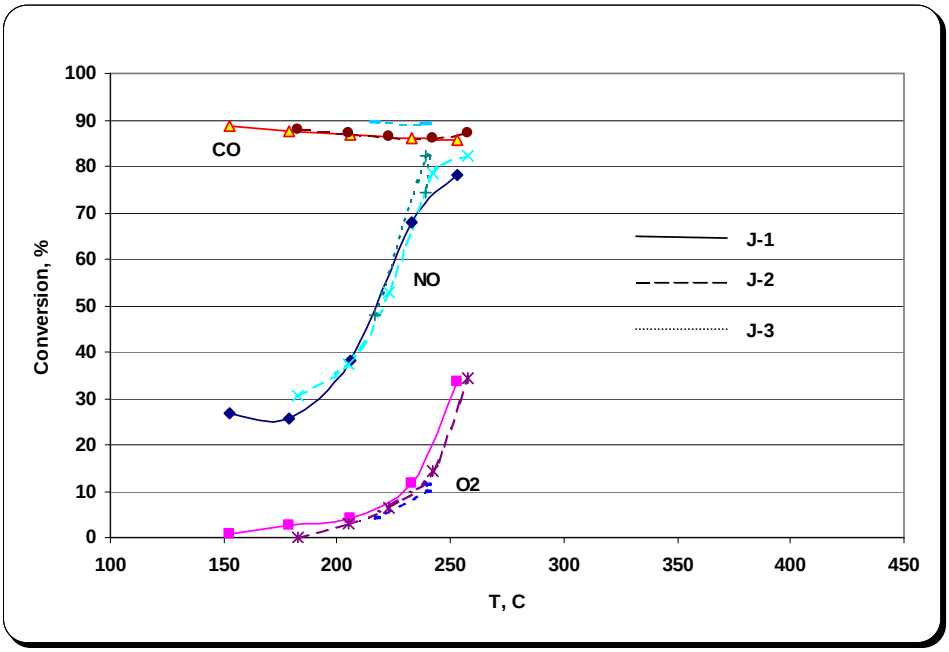

Figure 5 Conversion of gases

3.2 Base Line Tests with Activated Carbon

Active carbon has been reported to catalyze the NO reduction. For reference purpose, two un-promoted AC samples were tested. The first is the as-received AC. To determine the impact of our catalyst preparation procedure, a sample of the AC was aqueous-treated using the same procedure as used for the catalysts, except for using only distilled water without salts. The aqueous-treated AC was activated then in the same way as the other catalysts. The same operation conditions for testing catalyst were used, such as the GHSV and feed gas composition.

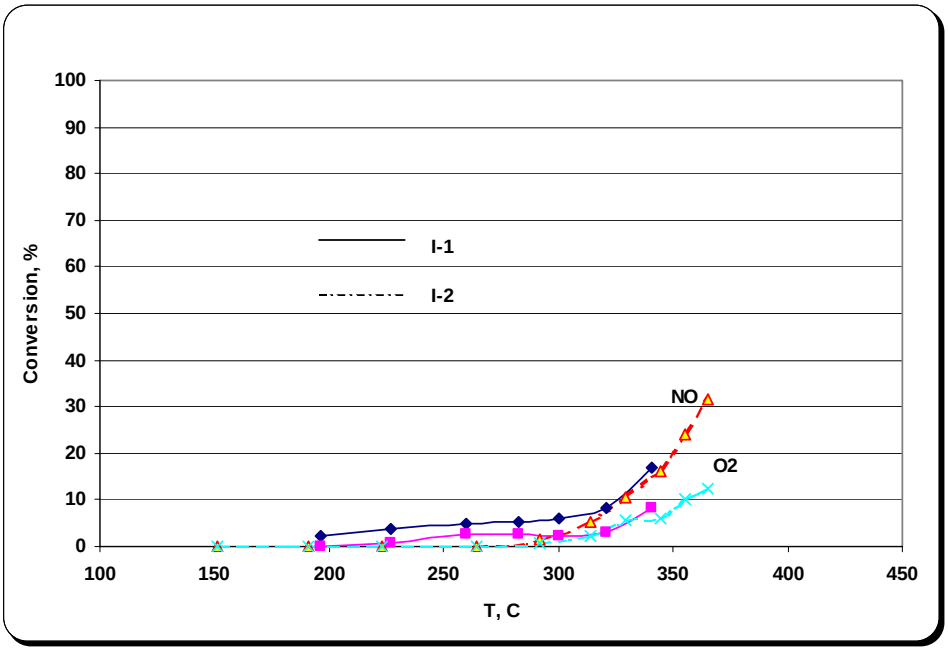

Figure 6 Baseline Test Data with Unpromoted AC (Catalyst-I)

As shown in Figure 6, the AC itself reduced very little NO at temperatures below 300°C. Similarly, little O_2 was consumed by reaction with carbon. As the temperature increased, CO was generated over the AC. At about 340°C, the CO in gas had doubled over inlet concentration, and the NO conversion increased too. Meanwhile, the O_2 consumption started to rise, indicating the AC direct combustion or partial combustion had occurred. It can be concluded that there is a link between the NO reduction and carbon partial combustion (oxidation), which is consistent with the so-called low temperature regime of NO carbon reaction in the literature (3,4).

No N_2O was formed for the reference AC test shown in Figure 6.

The NO conversion data for aqueous–treated and as-received AC are plotted in Figure 7. There was no significant difference between the as-received AC and the aqueous-treated AC. For NO reduction by AC, there was a small difference between day one and day two tests (A-1 and A-2) for the as- received AC, but A-2, and I-1 and I-2 were very similar. The reference AC samples (as-received AC, and aqueous-treated AC) had similar behavior during the testing.

The NO-carbon reaction can be boosted with presence of catalysts. The low cost of AC offers a very attractive option as catalyst support. The tested AC was made from lignite, and washed by acid to remove minerals. As a wet, fine-ground, high surface area powder (-100 Mesh, 1500 m^2/g), it contains less than 100 ppm Fe (according to the catalog) indicating that the samples used here contained little coal ash. Carbon burnout at the high temperatures needed for significant NO conversion and associated temperature runaway may limit the direct use of untreated AC for NOx reduction. However, if and where the carbon consumption is permitted, the direct NO-carbon reaction and reaction of NO with CO generated from AC can be beneficially utilized as part of the overall NO control process.

Another significant observation is that there was no CO reduction by the reference AC samples, as confirmed by repeated tests with both AC samples.

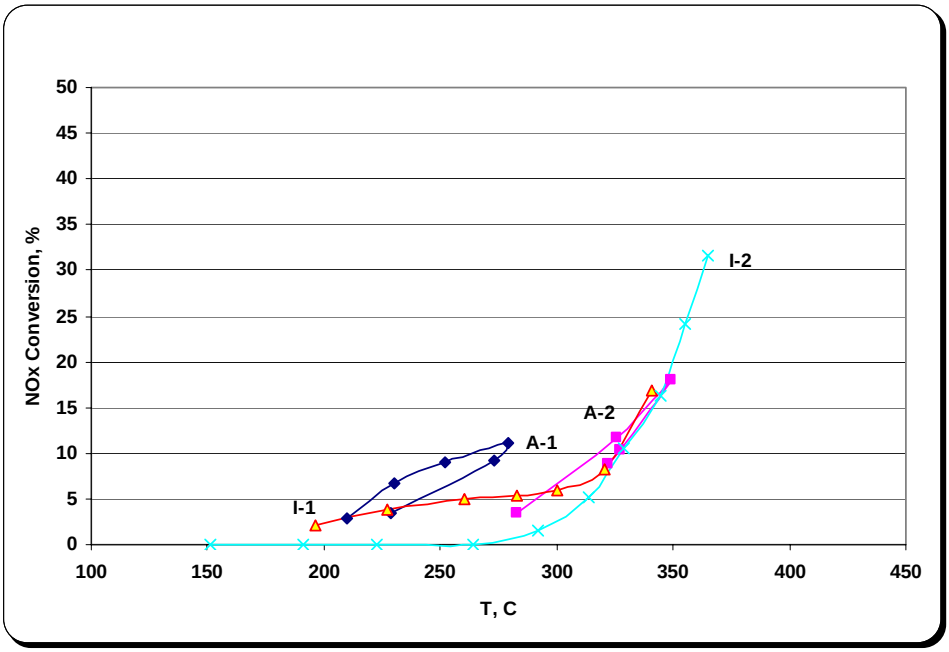

Figure 7 As Received vs Aqueous Treated AC

3.3 Fe Effect

Iron's potential as a NO reduction catalyst stems from its effectiveness as a catalyst for carbon gasification and combustion. The effect of Fe and its oxides as active components on catalytic reaction of NO-CO has been investigated. It was found to catalyze NO reduction by carbon or CO through a redox (reduction and oxidation) mechanism.

As reported by literature (2,5), Fe is a good catalyst for both coal gasification and combustion by enhancing the carbon reaction through different reaction pathways. The enhancement lowers the reaction activation energy, reaction temperature and NOx generation. It is of interest to analyze

the contribution of the catalytic effect by Fe in a group of Fe/Cu/AC catalysts. The tests for Fe loading effect, therefore, were prepared and carried out with different Cu levels.

The first effect, as shown in Figure 8, is that the addition of Fe on AC improved catalyst reactivity. The NO reduction reached over 70% as the temperature was increased to about 330°C. It shifted the catalyst bed temperature required for 50% NOx reduction (hereafter referred to as T_{50}) from 380°C for AC only (extrapolated from tested data range) to 320°C for the case with 40 % Fe loading. However, it was noted that even with Fe loading as high as 40%, there was no CO reduction for the Fe only cases. As the bed temperature increased, the CO generation started at about 270°C, and increased rapidly at about 330°C. O_2 was consumed as CO concentration increased. Thus, a large surplus of CO relative to needed amount for NO reduction resulted. It was also noted that the O_2 consumption was much higher than the stoichiometric amount required for CO generation, indicating the dominant combustion product was CO_2. The significant release of both CO and CO_2 as a consequence of carbon partial combustion verifies that although Fe is a good catalyst for the carbon gasification and combustion, it does not have any catalytic function for the CO reduction. The NOx reduction here is through NO - char reaction enhanced by Fe as catalyst. Evidently, the support carbon is involved in the NO reduction by CO. Further discussions on the effect of Fe on partial combustion and CO generation are included section 3.4 – Cu Effect.

In comparing with other supports, such as TiO_2, ZrO_2, Al_2O_3, and SiO_2, as reported in literature for iron oxide catalyst, where the N_2O is favored at low temperatures, the present AC supported iron oxide catalyst shows very good selectivity with little N_2O formation.

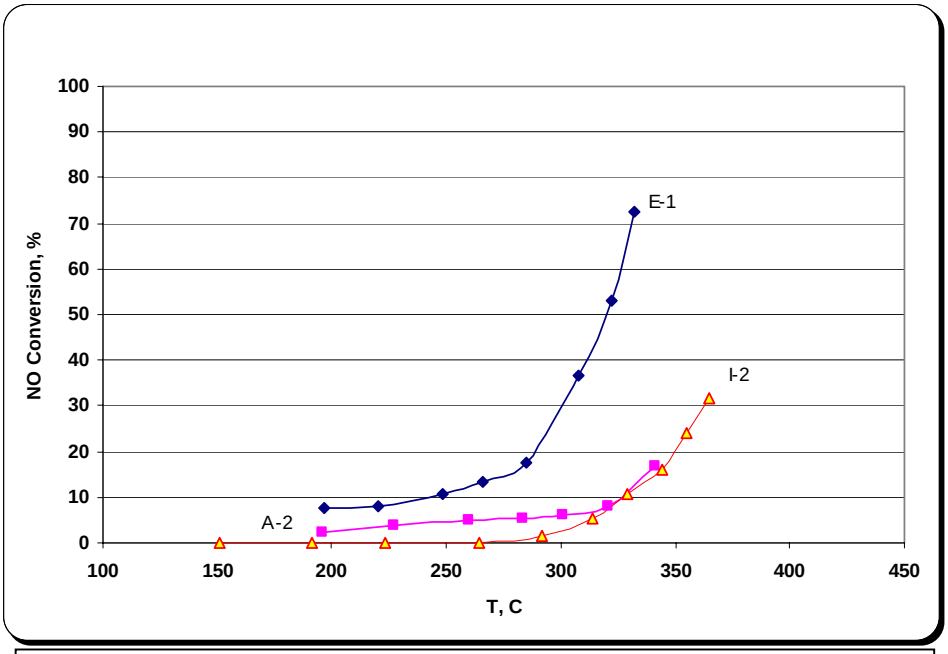

Figure 8 Fe Effect on Catalysts without Cu

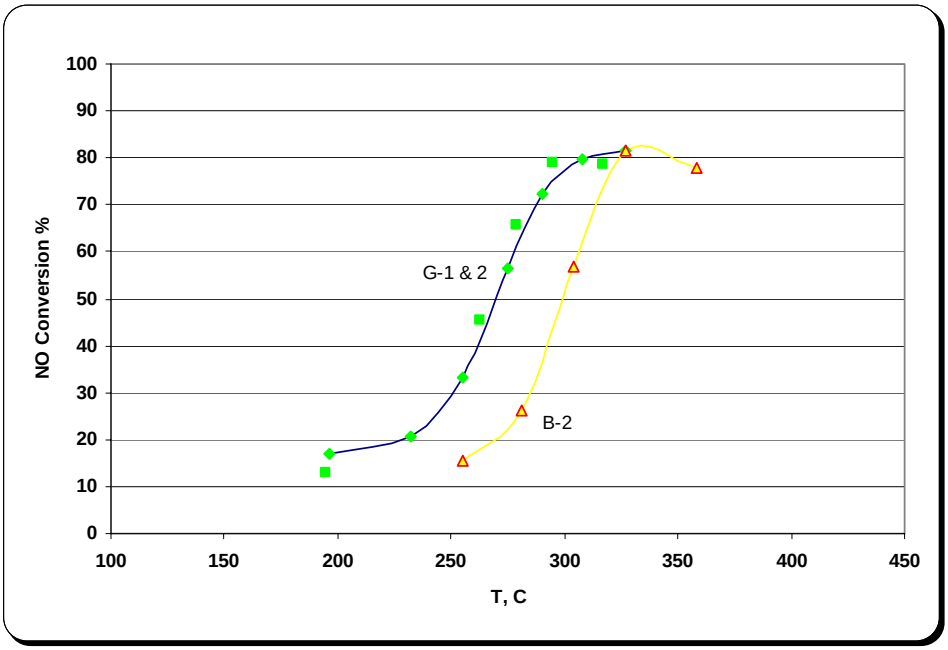

Figure 9 Fe Effect on Catalyst with 10% Cu

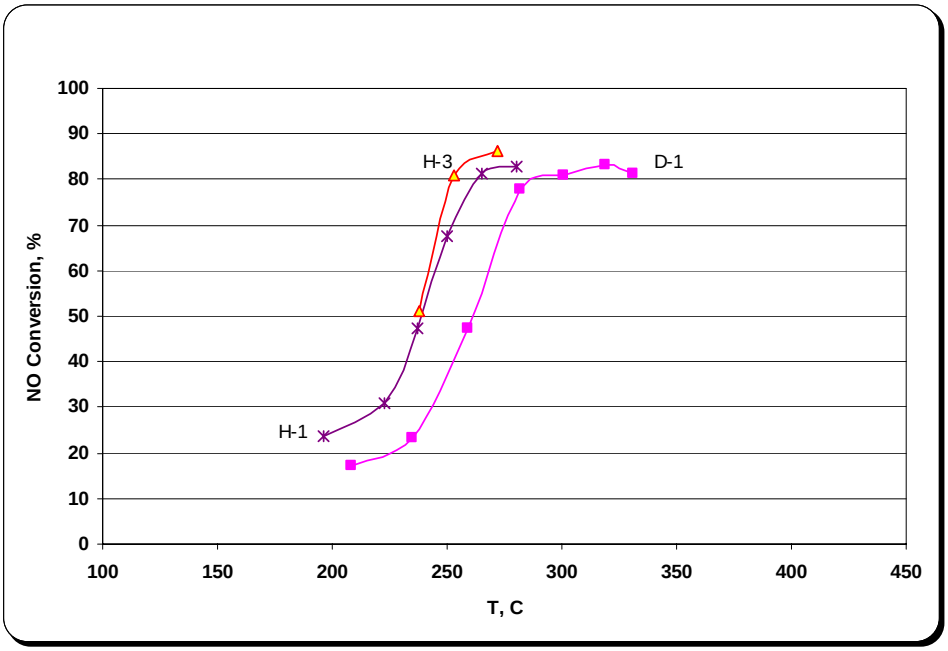

Figure 10 Fe Effect on Catalysts with 30% Cu

As a part of planned catalyst test, Cu was added to Fe/AC catalyst. As shown in Figure 9, with addition of 10% Cu loading on 40%Fe/AC, the index temperature T_{50} was again shifted lower, from 320°C to 270°C, compared to a shift from 380°C to 320°C when 40% Fe is added to the activated carbon. The maximum NO conversion also increased as Fe increased at given Cu=10% condition. A notable CO depletion was observed for both 10%Fe/10%Cu and 40%Fe/10% Cu cases.

To explore the effect of Fe on catalyst performance under high Cu loading, the Cu loading was increased from 10% to 30%, a further reduction in NO was obtained. The index temperature was shifted down further from 270°C to 240°C (Figure 10). Each time, for a given Cu loading, the increase of Fe loading enhanced catalyst reactivity, both in lowering T_{50} and in increasing the maximum NOx reduction. It is also very interesting that the CO was depleted this time at Cu=30% conditions for a wide range of temperatures. This effect on CO will be further discussed in the next section.

A high temperature excursion during test D-1 shown that the level of NO reduction hardly changed in the 308-365°C range, remaining relatively constant at above 80%. However the high temperature led to high CO generation. It apparently caused the formation of some reddish iron oxide on the catalyst, but no deactivation of the catalyst was observed.

As discussed so far in this section, the catalyst reactivity increased and T50 decreased as combined catalyst loading of Cu and Fe increased . However the benefit diminished as more metals were loaded. This total loading effect will be further discussed in a later section.

An important finding was that the addition of the Cu changed the reaction pathway. It showed that the Cu depleted CO. Therefore the NO reduction by CO must have involved a surface reaction between Cu and the adsorbed CO.

3.4 Cu Effect

It has been discussed that NO reduction by CO needs the support step from Cu. Without Cu, apparently, the CO could not react with NO even with the presence of Fe. Commercially, Cu has been used as catalytic agent for synthesis of CH_3OH from syngas, $CO+H_2$. Copper chloride solution has been used as chemical solvent for the CO removal from H_2 gas in ammonia plant. Cu salts supported on AC were found to be more reactive than on other supports at low temperatures.

The loading effect of Cu on catalyst performance was further investigated. Three catalysts with different Cu loading, (Cu=0%, Cu=10% and Cu=30%) were made for a constant Fe=40%. As expected, the test results showed that the catalyst reactivity increased as the loading of Cu increased (Figure 11 and Table 2):

Table 2 Impact of Cu Loading on T_{50}

Cu, Loading ,%	0	10	30
$T_{50,}$ °C	320	270	240

It was noted that the maximum NO reduction also increased when Cu loading increased for a fixed Fe=40%.

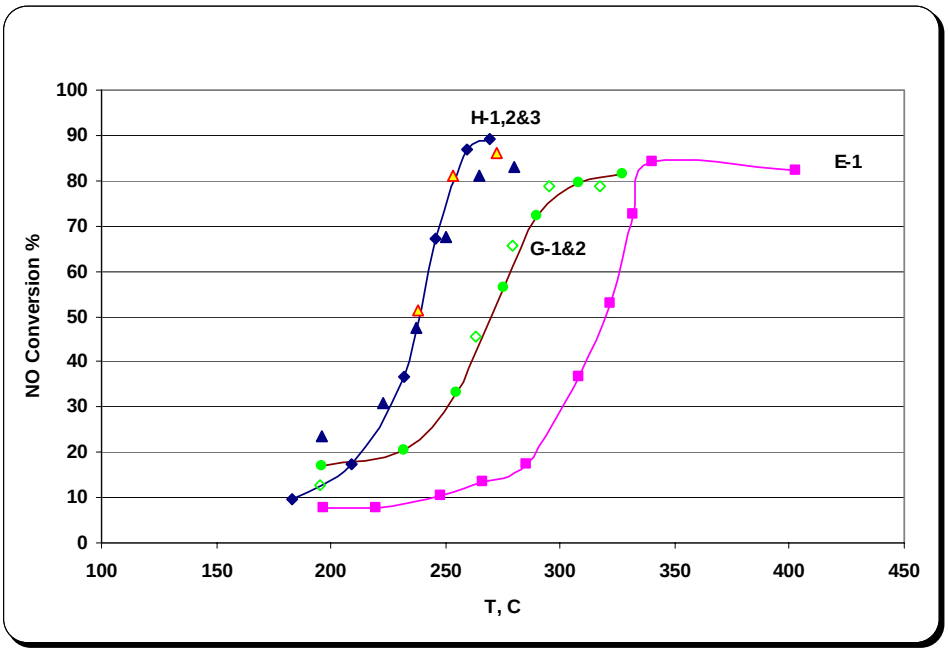

Figure 11 Cu Effect on Catalysts with 40% Fe

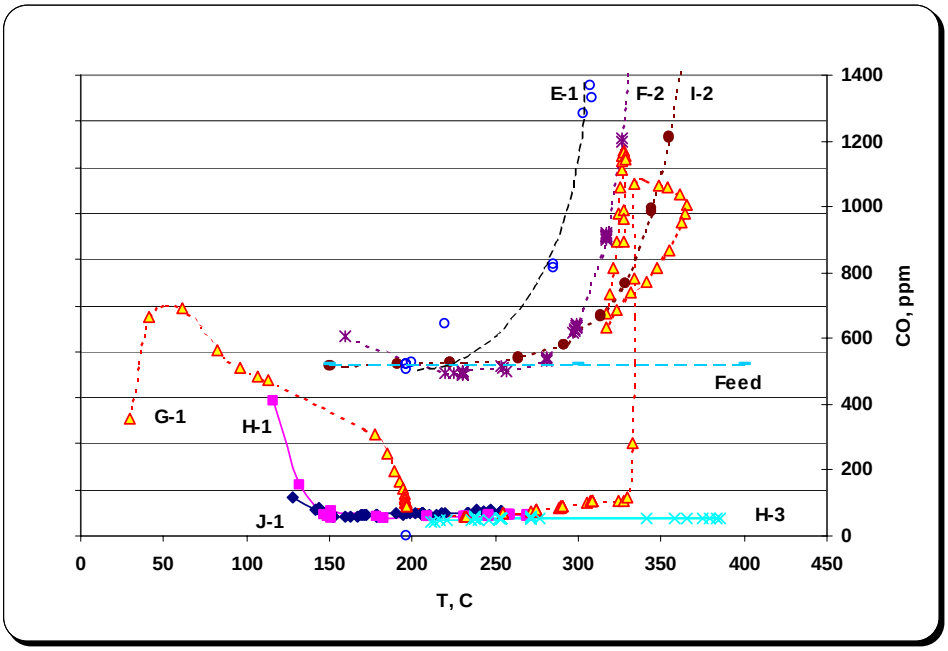

Figure 12 CO Concentrations for Different Catalysts

As mentioned earlier, Cu plays an important role in CO reduction. The NO reduction by CO involved a surface reaction between Cu and the adsorbed CO. As shown by transient data in Figures 4 and 12, for catalyst-H with a high Cu loading (30%), CO reduction was as high as 87 to 90% for the entire test temperature range up to 390°C. However for catalyst-G with 10% Cu, CO started to shoot up as temperature approached 330°C. CO initially was depleted at low temperatures. As temperature increased, CO started to be generated by Fe catalyzed carbon combustion. The catalysts E & F, with no Cu or very low Cu, behaved the same way as the AC only cases, with no CO depletion even at very low temperatures.

At even lower temperatures (Figure 12), initially the adsorbed CO on AC support was released, and shortly after that when temperature is high enough to activate the CO depression reaction, CO concentration rapidly dropped to below 50 ppm for the Cu containing catalysts G, H and J.

There are two competing reactions between CO generation promoted by Fe, and CO reduction promoted by Cu. This competition is affected by bed temperature. High bed temperature enhances the catalytic conversion of carbon to generate more CO and CO_2, while the high Cu loading enhances the CO deletion. The optimum composition of catalyst should address both reaction pathways. For operation at increased temperatures, the Cu loading needs to be increased. To ensure low levels of CO emissions, a low operation temperature and a relative high loading of Cu are necessary.

3.5 Ce Effect

In general, the studies (3) show that the Fe and Cu are the most effective catalyst components for NO reduction by carbon or by CO. Ce had been reported to enhance catalytic redox processes. Cerium is widely used in automobile three-way catalyst as an oxygen transferring agent due to its redox behavior.

The tested data plotted in Figure 13 showed that the addition of 20% Ce (catalyst-J) increased the catalyst reactivity, compared with catalyst-H. T_{50} was lowered further to 210-220°C. It was also noted that the O_2 consumption "light off" temperature was reduced by 15 to 20 °C. There were no changes in CO depletion by adding Ce to the Fe/Cu/AC group. Because the addition of Ce increased the total loading, it showed the similar reactivity trend as catalyst loading of other metals (Fe and Cu) increased. It appears that the Ce boosted the reactivity more on the low temperature side. Appreciable NO conversion was observed at reaction temperatures below 200°C. This high loading catalyst results in a very low operation temperature, and therefore it greatly suppresses the CO generation. However, the O_2 consumption data of catalyst J appears to indicate predominately CO_2 generation at low temperatures and the lack of significant CO generation may be due to the high Cu loading, and possibly the Ce application.

No special characteristics were found at this time from Ce addition except that it enhances the catalyst reactivity in a similar way as Cu and Fe. The literature has reported that the addition of Ce dramatically improved the selectivity to N_2 during NO reduction. However, the present test data showed that a very good selectivity to N_2 was achieved even without Ce. Therefore, Ce does not bring distinct benefits to the catalysts tested so far, especially considering its price is higher than Cu and Fe.

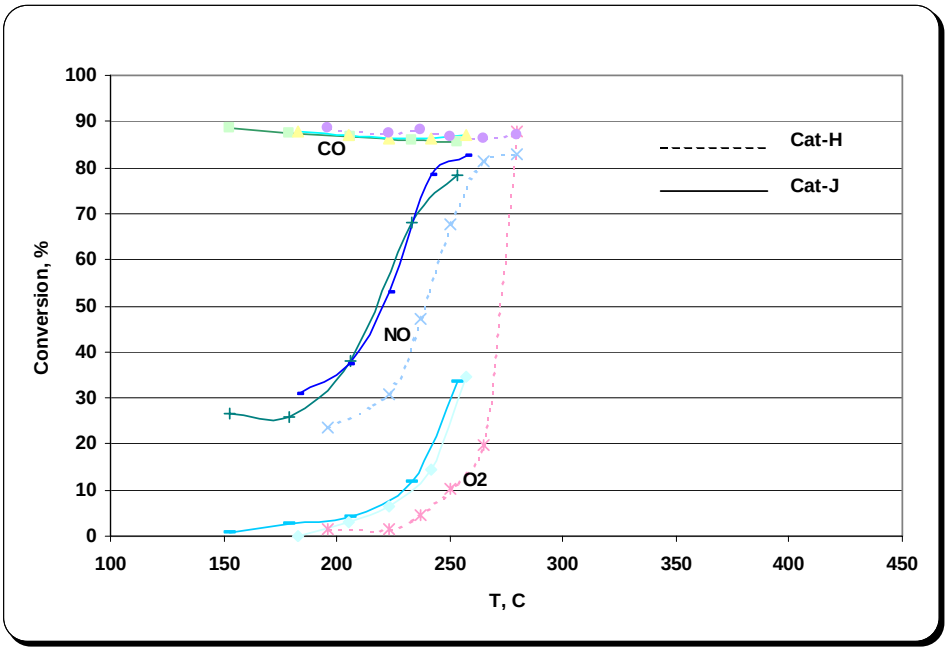

Figure 13 Effect of Ce on Catalyst Performance

3.6 Loading Effect

As discussed earlier, the catalyst reactivity increased as its total loading of metals increased.

A new parameter of total loading, i.e. Fe+Cu+Ce, has been used to analyze its effects on the catalyst reactivity. In general, the test result showed that the catalyst reactivity increased as the total loading increased even as contributions from Cu, Fe and Ce were different (Figure 14). In general the maximum NOx conversion increased as total loading increased, except for the case with Ce addition (J-1). Although J-1 exhibited a lower T_{50} and had an initial reduction of close to 30% at low temperatures, it did not have high maximum NO reduction.

It should be pointed out that the contribution or effectiveness of different metal component is different. Some catalysts had better performance than others with the same or even higher total loadings. As shown in Figure 15, catalyst-B with low total loading (10% Fe and 10% Cu) was more active than the catalyst-E with higher total loading (Fe+Cu=40%+0%). The same is true for the comparison between catalyst-D (Fe+Cu=10%+30%) and catalyst-G (Fe+Cu=40% +10%). It tells us again that Cu played important role in NOx by CO by altering the reaction pathway as discussed earlier.

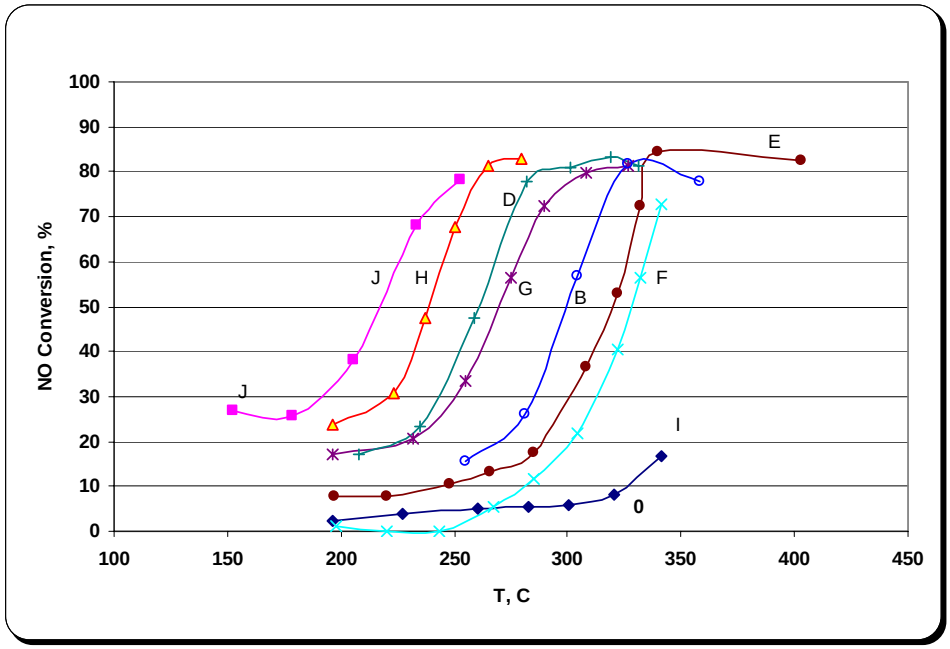

Figure 14 NO Conversion Performance for Various Catalysts

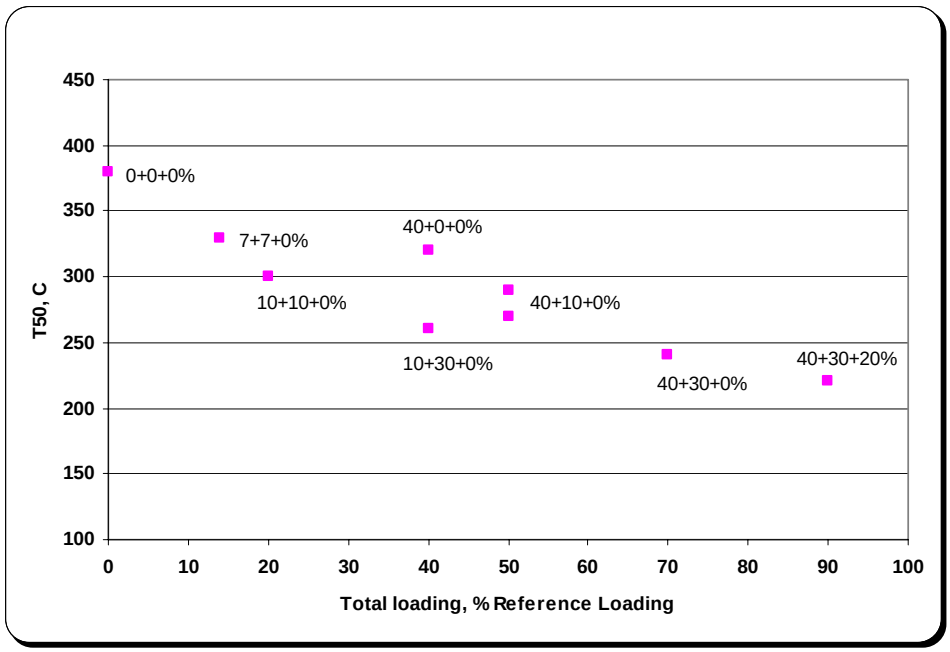

Figure 15 Effect of Total Loading on Reactivity Index T50

3.7 N_2O Generation

N_2O emissions were measured for the tests performed in May and June, including catalysts E, F, G, H, I, and J. As plotted in Figure 16, overall the NO to N_2O conversion was small, with the highest measured N_2O conversion at only 12 %. The reference AC (I) did not generate any N_2O through the entire temperature range. Other catalysts with metal loading did convert some NO to N_2O, and the conversion increased with increasing catalyst bed temperature. Another clear trend seen from the data in Figure 16 is that the catalysts with higher total metal loading tend to generate more N_2O and at lower temperatures.

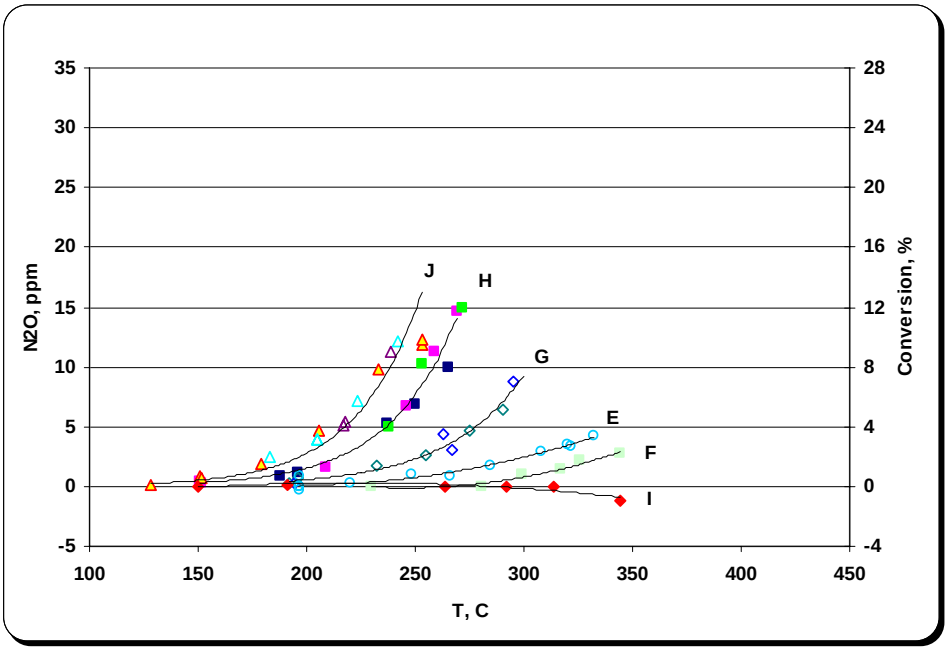

Figure 16 NO to N_2O conversion

3.8 O_2 Consumption

The catalyst with the lowest metal loading (Type F, 7% Fe / 7% Cu) was selected to investigate the effect of initial small loading on activated carbon. For this low loading catalyst, the maximum NOx reduction occurred at about 350°C. Similar to the reference AC only tests, as temperature exceeded 270°C, the NOx-carbon reaction started as a result of the support AC burning. The familiar "light off" was seen for this low loading catalyst, as with the reference AC only case (Figure 12). As shown in Figure 17, O_2 concentration and CO generation were in sync. However, since the initial O_2 concentration and its consumption were orders of magnitude higher than the initial CO concentration in the feed stream, clearly most of O_2 was consumed by partial combustion of carbon to generate predominantly CO_2, as well as more CO.

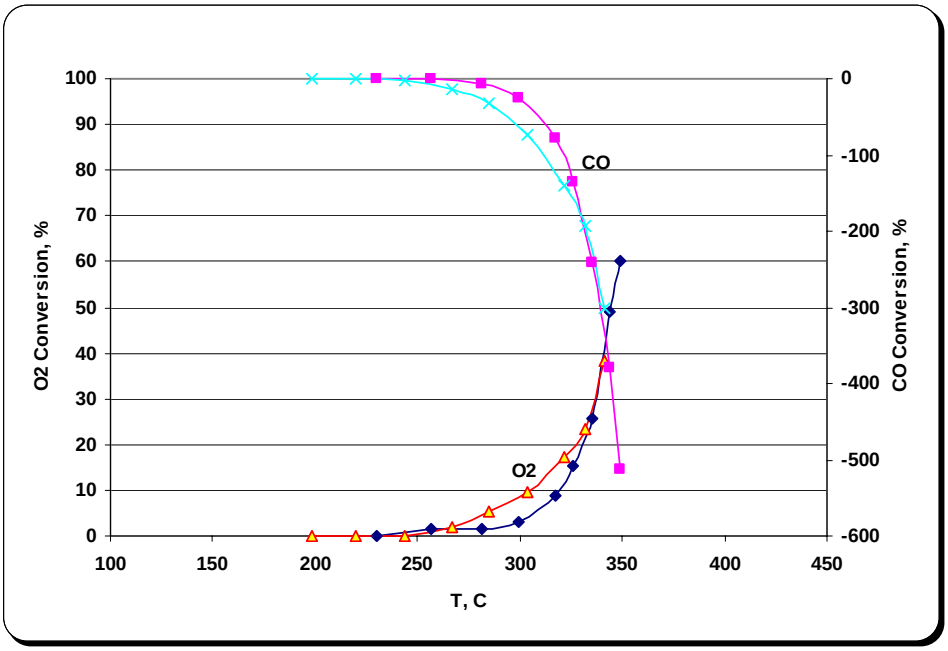

Figure 17 CO and O2 Conversions for Catalyst F

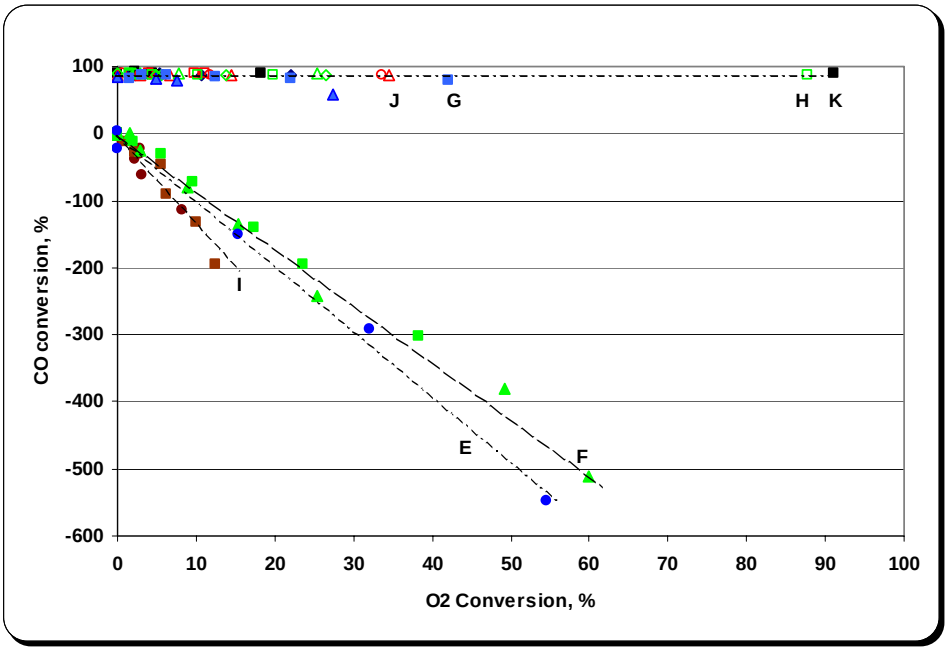

Figure 18 Relationship between CO and O_2 Conversions

Figure 18 shows that the CO generation and O_2 consumption occurred simultaneously for low Cu catalysts E and F , as indicated by linear relations in the figure. On the other hand, with high Cu loadings (catalysts G, H, and J), there was excellent CO reduction for a wide of operation temperature range from 150 to 380°C.

There were clearly two categories of the relationships between conversions of CO and O_2. For reference AC only and low Cu catalysts, CO generation was proportional to the amount of the O_2 consumed (Figure 18). For the high Cu catalysts, the CO conversion stayed at 80-90% of the feed concentration regardless of O_2 consumption by carbon, which means with these catalysts, the carbon reaction was nearly complete to produce predominantly CO_2. In Figure 19, one can see that the carbon combustion (as indicated by O_2 consumption) was promoted by the total metal loading. However, for the high loading catalysts with sufficient Cu, even with significant carbon burning, the CO level still remained very low.

In summary, the catalysts with sufficient Cu loading reduced CO by more than 85% in a very wide temperature range. This is a very important feature since some carbon burning is expected when AC support is used.

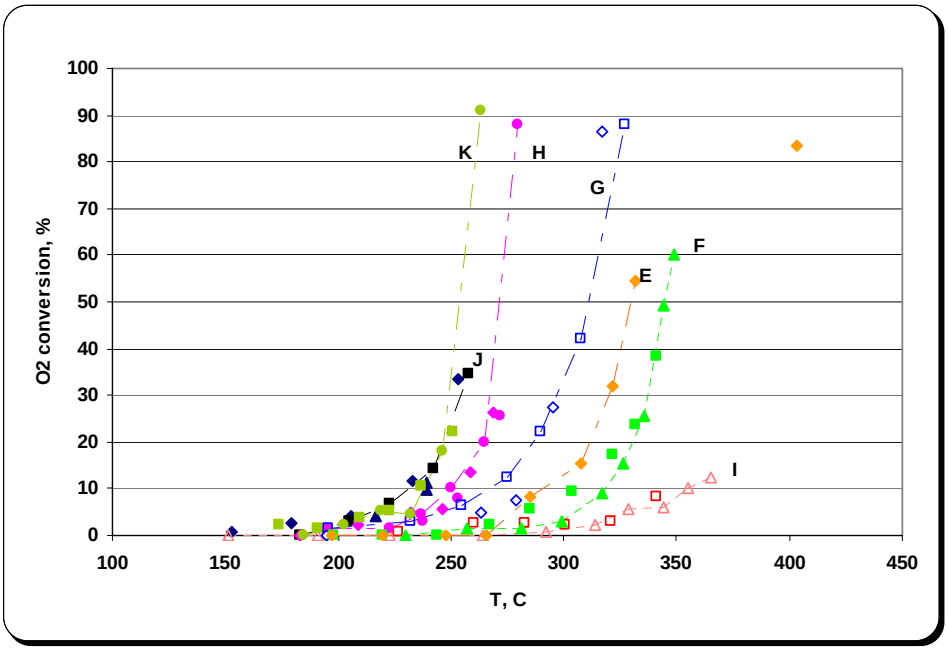

Figure 19 Effect of Catalyst Type on O2 Conversion

3.8 Catalyst Stability

Some of the catalysts were tested for longer durations under constant conditions to check their stability.

As shown in Figure 20, the stability of the catalyst D was demonstrated by operating at 275°C under steady state conditions for nearly 12 hours. The system was well operated and maintained at a steady state condition with approximately 86% NO reduction. No significant reactivity decay was seen during the test.

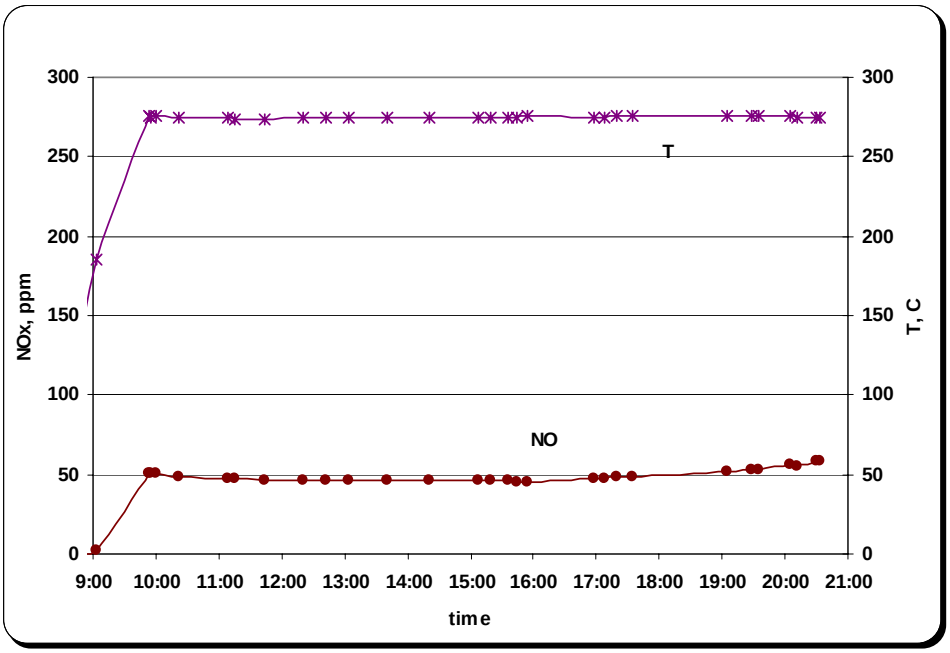

Figure 20 Long Duration Test at Constant Conditions

4. Conclusions

Activated carbon can cause NO conversion through direct reduction by carbon, or by CO. The latter reaction pathway is assisted by the partial combustion of carbon that delivers CO, along with CO_2. However, temperatures as high as 500°C or more is needed for effective NO conversion with untreated AC. At such high temperatures, excess consumption (burning) of AC will be inevitable and CO emissions will reach unacceptable levels.

The experimental work of the current quarter proved that depositing transition metals in mono-, bi-, or ternary metal-oxide forms on activated carbon support resulted in higher NO conversion at lower operation temperature ranges, thus avoiding excessive consumption of support AC and CO generation.

The catalyst preparation procedures used in this work preserved the micro pore structure of the activated carbon. The deposit of metal ingredients caused only minimal reduction in the specific surface area.

Although precious metal catalysts have been successfully applied in the automobile industry to convert NO with CO and hydrocarbons as reductants. Those catalysts require a reducing environment as typically found in the gasoline engine exhaust, and therefore are not suitable for power plant flue gas applications, where oxidizing conditions must be maintained for safety and efficiency considerations. The group of base metal catalysts, prepared and tested in this study, generated very promising NOx conversion under simulated power plant flue gas conditions, including 3% oxygen. This is a crucial step towards a practical, ammonia-free, catalytic NOx reduction system for combustion power plants.

Other significant findings from the testing for the group of Fe/Cu/Ce/AC catalysts include:

- NO reduction reactivity increased as the total loading of metals increased, which included Fe, Cu and Ce.
- NO reduction in the range of 80-90% was achieved in multiple repeat test runs with several metal / loading combinations, and with operating temperature ranging from 250°C to 350°C.
- Different catalytic functions of metals were observed: Fe on AC appeared to promote carbon gasification and combustion, while Cu helped the CO conversion (oxidation) to levels as high as 90%.
- Optimum Fe/Cu/Ce ratio was evaluated by considering competing reaction pathways between reactants of carbon and CO.
- The test data have shown excellent NO to N_2 selectivity. The measured NO to N_2O conversion was in the range of 0-12%; and the conversion was strongly dependent on the combination of metals used.
- Stability testing for 12 hours under constant conditions exhibited continuous and high NO conversion (86%) without noticeable reactivity decay.

In summary, the AC supported base metal catalysts have shown very promising NOx conversion and selectivity in oxidizing environment with CO as reductant. In the coming months, these catalysts will be subjected to longer duration testing and exposed to feed gas including SO_2 and moisture to determining their resistance to poisoning and inhibition. The same base metals will be applied on non-carbon based substrate to explore catalysts with more durable physical structure.

5. References

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